

Recycling of Dry and Wet Polyamide 6

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ABSTRACT: Recycling of polycondensation polymers can give rise to secondary materials with good mechanical properties only if a careful drying is carried out before the melt reprocessing operations. The presence of humidity provokes the hydrolytic chain scission of the macromolecules and the consequent decrease of molecular weight and properties. In this work, the drying step was substituted by the addition of

an antioxidant that is able to protect the macromolecules because it is the antioxidant is more prone to hydrolysis, thus removing the water from the melt. The mechanical properties of polyamide 6 reprocessed more times in wet conditions and in the presence of this stabilizer are even better than those obtained reprocessing the dry polyamide. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1899–1903, 2002

INTRODUCTION

Mechanical recycling of polymers is a very complex and difficult process because repetitive melt processing can lead to severe degradation of these materials with subsequent deterioration of all the properties.^{1–6}

The thermomechanical degradation undergone during melt processing operations can be slowed or avoided by adding small amounts of stabilizers that act on the radical propagation reactions or on the reactions of the hydroperoxide compounds formed during processing in the presence of oxygen.^{7–14}

For condensation polymers, the degradation rate is much faster in the presence of water that induces depolymerization reactions, having also a synergistic effect with thermomechanical degradation and exalting the loss of the properties. In this case, a careful drying is the necessary step before the melt operation but, of course, it is complicated and increases the costs of the recycling. To avoid this problem, different techniques are used to remove water and oxygen from the processing machine,^{15,16} or to add molecules able to extend the molecular weight of the polymer.¹⁴ Under these conditions, not only it is possible to preserve the initial molecular weight, but even to obtain an increase of it, due to the chain extension.

The aim of this work is to study the effect of the reprocessing of a molten polyamide 6 samples with and in the absence of water in view of the mechanical

recycling of this polymer. The effect of an antioxidant was also investigated. This antioxidant is able to protect the polyamide when reprocessed in wet conditions because it is more prone to the hydrolysis, so it removes the water from the molten polymer.

EXPERIMENTAL

The material used in this work was a sample of polyamide 6 (PA6) supplied by Rhodia (Italy) with a relative viscosity (measured in sulfuric acid) of 3.8 dL/g.

An antioxidant, a high molecular weight phosphonite compound, Sandostab P-EPQ (Clariant), whose formula is tetrakis-(2,4-ditert-butylphenyl)-4,4'-biphenylylen-diphosphonite, was added in some extrusion tests at a concentration of 500 ppm.

Recycling operations were performed by using a single-screw extruder Brabender Plasticorder model PLE 651 (L/D = 25, D = 19 mm) equipped with a flat die. The thermal profile was 240–240–240–240°C. To simulate recycling operations, the materials have been processed up to five times.

Extrusion tests were carried out on dry and wet samples. In the first case, the polyamide was dried in a vacuum oven for 24 h at a temperature of 120°C. Tests on wet PA6 were performed on materials left for at least 120 h at room temperature and room humidity, enough to ensure an almost complete humidification of the polyamide. The stabilizer was never dried before use.

Characterization

Rheological measurements were performed by using a Rheometrics RDAII parallel plate rheometer on samples with a diameter of 25 mm cut out from compression-molded sheets. All the samples were carefully

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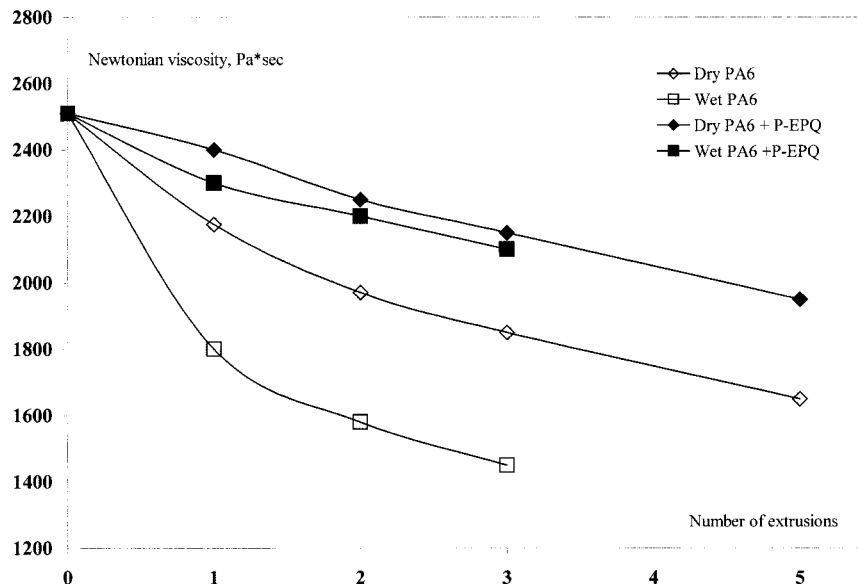


Figure 1 Newtonian viscosity of samples reprocessed in wet and dry conditions as a function of the number of passages in the single-screw extruder.

dried before measurements to prevent further hydrolytic chain scission during the test.

Mechanical properties were measured with an Instron 1122 tensile testing machine on samples cut out from compression-molded sheets. The results reported here are the average of at least 10 measurements and have been carried out on wet samples. In both cases, the sheets were obtained by dry materials to reduce any postprocessing degradation effect.

Heat of fusion was measured by using a differential scanning calorimeter (DSC-7; Perkin-Elmer).

RESULTS AND DISCUSSION

The flow curves of all the samples, here not reported, present only a small variation with the shear rate. Because, as it is known, the thermomechanical treatment mainly influences the value of the Newtonian plateau, in Figure 1, the Newtonian viscosity of samples reprocessed in wet and dry conditions, as a function of the number of passages in the single screw extruder, is reported. The Newtonian viscosity of the stabilized samples was also plotted. As for the unstabilized samples, the dry sample shows a Newtonian viscosity larger than that of the sample processed without drying. As for the effect of the reprocessing operations, the viscosity of the wet unstabilized sample undergoes the largest decrease: after only three extrusions, the viscosity drops from about 2500 Pa·s to about 1400 Pa·s. The Newtonian viscosity is a strong function of the molecular weight, according to the equation:

$$\eta_0 = KM_w^{3.4}$$

where η_0 is the Newtonian viscosity, K is a constant dependent on the temperature, and M_w is the molecular weight. This means that after three extrusions, in these processing conditions, the molecular weight of a wet nylon sample decreases about 20%. The situation is less dramatic if dry PA6 is used: after three extrusions, the dry PA6 shows a viscosity higher than that of wet PA6 after one passage in the extruder. After five passages, the viscosity is still higher than that of the two times extruded wet sample and the change of molecular weight is about 12%. As already said, the decrease of the Newtonian viscosity of the sample reprocessed after drying is clear evidence of a reduction of molecular weight due to thermomechanical stress acting on the melt. For the wet sample, the effect of the thermomechanical treatment is strongly enhanced by the hydrolytic chain scission provoked by the presence of the humidity.

The behavior of the two samples is completely different when P-EPQ is used. In both cases, the viscosity is higher with respect to the same unstabilized samples. The quantitative effect is, however, different if the sample is processed with or without drying. In particular, the curves relative to dry and wet samples tend to superimpose in the presence of the stabilizer. This result is surprising considering that one of the two curves refers to a sample reprocessed without drying. As it can be clearly observed in Figure 1, both samples still show a reduction of viscosity with increasing the number of extrusions, but this reduction is more contained. In particular, the stabilized dry PA6 has a viscosity about 15% higher after three and five extrusions, whereas the wet stabilized sample has a

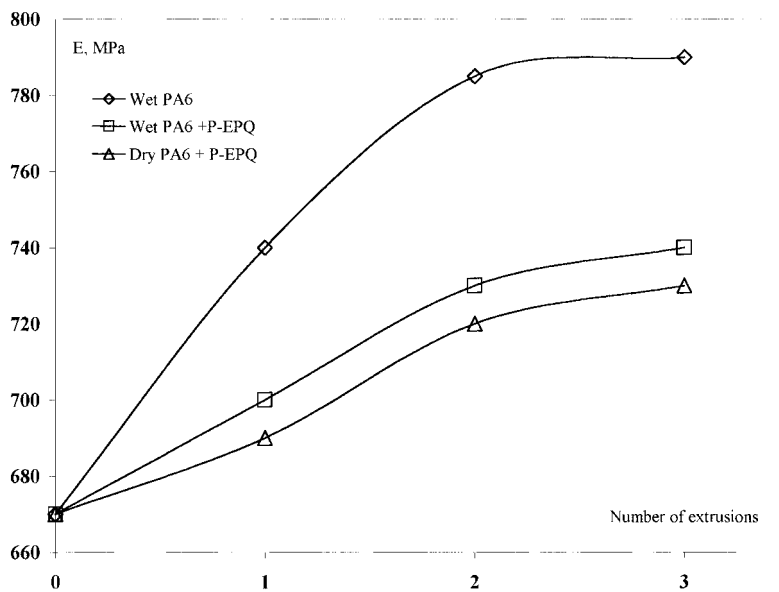


Figure 2 Tensile stress as a function of the number of extrusions.

viscosity 50% higher than the respective unstabilized material.

The improved behavior of the dry polyamide in the presence of this antioxidant during the reprocessing operations was explained, in previous articles,^{17,18} hypothesizing that the P-EPQ phosphonite is very prone to hydrolyze, so removing water from the bulk. As PA6 is sensible to water, the stabilizer removing the water from the processing environment protects the melt from hydrolytic chain scission.

Mechanical properties

The results coming from the mechanical measurements confirm what already was discussed.

In Figures 2 and 3, the tensile stress, TS, and the elongation at break, EB, are reported as a function of the number of extrusions for all the investigated PA6 samples.

For the dry and P-EPQ-stabilized samples, the change of the tensile stress values (Fig. 2) is very small and after three extrusions the tensile stress of all these samples is absolutely comparable with the value measured for the virgin and the neat dry PA6. Also, for the elongation at break (Fig. 3), the situation is similar. The P-EPQ-containing samples show the lowest reduction of this property, whereas wet unstabilized PA6 shows worse behavior. In particular, the wet sample and the dry polyamide after three and five extrusions, respectively, show an EB value of about

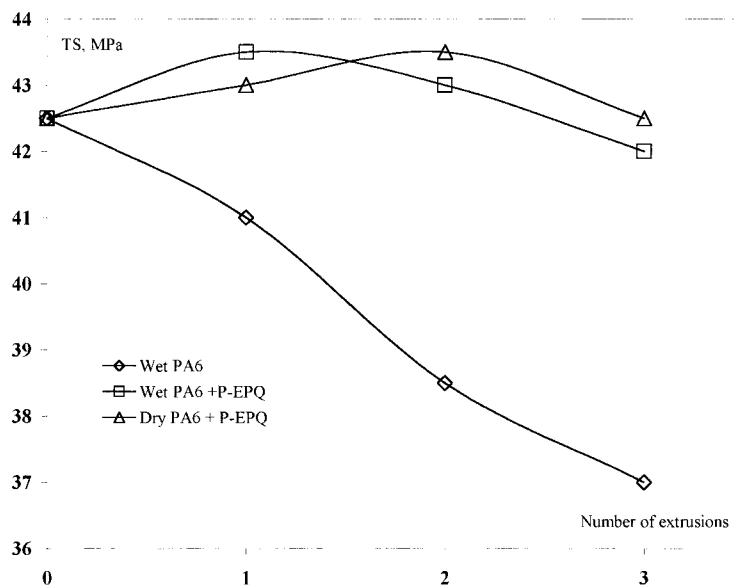


Figure 3 Elongation at break as a function of the number of extrusions.

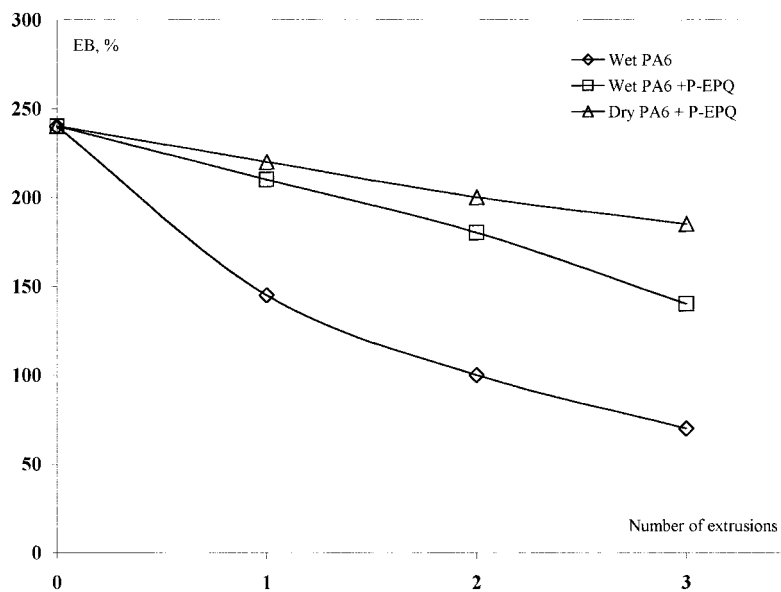


Figure 4 Elastic modulus as a function of the number of extrusions.

50%, that is, about one-fifth of the initial value. The decrease of the ultimate tensile properties is directly related to the reduction of the molecular weight already discussed for these systems.

A remarkable increase of the tensile modulus, Figure 4, on the contrary, can be observed for all the samples. In contrast with respect to the ultimate properties of the previous figures, the highest values are displayed by the unstabilized wet PA6. The lowest growth of the modulus is observed for the P-EPQ-containing sample, whereas the dry PA6 material shows an intermediate behavior.

Apparently there is a contradiction between the modulus measurements and the ultimate tensile stress values, as the reduction of the molecular weight should induce not only a reduction of tensile stress and elongation at break, but also a reduction of the elastic modulus. This behavior has already been observed for other semicrystalline polymers^{13,19} and was reasonably explained with the variation of crystallinity due to the processing. The thermomechanical stress and the hydrolytic scission cause a reduction of the molecular weight that implies an increase of crystallinity and then higher values of the elastic modulus.

The heat of fusion measured on some samples, Table I, confirms this hypothesis. By increasing the deg-

radation phenomena, the heat of fusion increases. This means that the crystallinity is larger because of the lower molecular weight.

The increase of crystallinity improves the elastic modulus and this increase is larger for the wet and unstabilized samples where the degradation is larger. The increase of crystallinity counterbalances the negative effect of the reduced molecular weight on the tensile stress, whereas it enhances the effect of the lower molecular weight on the elongation at break. Both factors, indeed, tend to reduce the ductility of the polymers. For this reason the elongation at break is the mechanical property more sensible to the degradation phenomena.

CONCLUSION

Repetitive processing of PA6 can give rise to secondary material with good properties only if a careful drying step is carried out before the melt operation. In these conditions, the rheological and mechanical properties are slightly changing by increasing the number of processing steps. The degradation is due to the thermomechanical stress acting on the molten polymer. Reprocessing of wet materials provokes, on the contrary, a drastic reduction of molecular weight by hydrolytic chain scission. The use of an additive able to remove the water makes possible the recycling of polyamide—and of other polycondensation polymer—also in wet conditions. The recycled material shows good properties even after many reprocessing steps.

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TABLE I
Heat of Fusion of Some Samples

Sample	Heat of fusion (J/g)
Virgin Ny	67.1
Ny, dry, 5 extrusions	78.7
Ny+P-EPQ, dry, 5 extrusions	73.7
Ny, wet, 3 extrusions	79.5
Ny+P-EPQ, wet, 3 extrusions	74.2

Rubber Processing Machinery and Molds Manufacturers Association).

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